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An all small molecule organic solar cell based on a porphyrin donor and a non-fullerene acceptor with complementary and broad absorption

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ARTICLE INFO	A B S T R A C T			
Keywords: Organic solar cells All small molecule Porphyrin Complementary absorption	A thieno[3,2- <i>b</i>]thiophene-functionalized porphyrin molecule (DEP-TT) with the ethynylene bridges between the diketopyrrolopyrrole and porphyrin units has been designed and synthesized as the donor material. DEP-TT exhibits a broad absorption wavelength in the visible region with the onset absorption to 898 nm of the film and a low optical band gap of 1.38 eV. IDT-C8 , as the acceptor material has a relatively strong absorption spectrum ranging from 500 to 750 nm in the solid film, which exactly fills the absorption trough of DEP-TT . The power conversion efficiency (PCE) of all small molecule increased from 0.64% ($J_{sc} = 2.61$ mA cm ⁻² , $V_{oc} = 0.82$ V, and FF = 0.30) to 5.14% ($J_{sc} = 11.15$ mA cm ⁻² , $V_{oc} = 0.71$ V, and FF = 0.65) after solvent vapor annealing. The PCE of 5.14% provided valuable recommendation based on porphyrin all small molecule system, since few work has			

1. Introduction

Solution-processed organic solar cells (OSCs) have extensively attracted significant attention in recent years due to their light weight, low cost and potential to fabricate flexible and large area panels [1-5]. In the past decade, with the advantages of high electron mobility and high electron affinity, fullerene derivatives PC61BM or PC71BM have been widely used as acceptors in the OSCs community [6,7]. Power conversion efficiencies (PCEs) of over 10% have been achieved for fullerene derivatives based on devices [8,9]. However, fullerene derivatives have the limitations such as weak absorption in the visible region, difficulty in tuning the energy levels and high cost for preparation and purification. Therefore, great attentions have been paid to the non-fullerene (NF) acceptors based OSCs. Various NF acceptors including polymer [10-12] and small molecule [13-15] have been designed and evaluated in OSC devices. Presently, among various types NF materials, A-D-A structure small molecule acceptors have shown the best device performances when blended with polymer donors and PCEs with breakthrough values over 16% have been achieved recently [16-20].

Due to the advantages, such as less batch to batch variation, easier energy level control and etc., small molecule donor materials have experienced fast development and demonstrated great progress in recent years [21-24]. Comparable and even more promising device performances have been realized for small molecule donors/PCBM based OSCs in contrast to their polymer counterparts. However, the study of small molecule donors/NF OSCs, especially all small molecule devices, have greatly lagged behind that of polymer donors/NF OSCs [25-28]. Unlike PCBM, small molecule acceptors, especially those A-D-A type acceptors, have anisotropic conjugated backbones and the molecule packing modes greatly influence the charge transport behaviour. In addition, they tend to have good miscibility with small molecule donors, especially A-D-A type donor molecules owing to the similar chemical and electronic structures, which led to the unfavorable phase separation and hard controlled morphologies [29-32]. Thus, it is indeed challenging to achieve high efficiency in all small molecule OSCs. To this end, it is necessary to synergistically design and evaluate the donor and acceptor small molecule from the perspective of their absorptions, energy levels and blending film morphology control, etc. [33] In recent years, much progress has been made for all small molecule OSCs through careful

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small donor/acceptor molecules design and device optimizations. For example, Hou [34] and Li et al. [35,36]. have reported series of all small molecule OSCs with PCEs around 10% through delicate small molecule donor design and device optimization. Recently, Wei and Zhu et al. have reported ternary OSCss based on all small molecules and demonstrated promising PCEs 13-14% [37,38]. Considering the success in small molecule, especially A-D-A donor molecule based devices with PCBM, all small molecule OSCs are strongly believed to have an exciting opportunity offering comparable and maybe even better performance compared with polymer donor based devices. To this end, suitable donor/acceptor small molecule design and active layer morphology control play the vital role. In contrast to the comprehensive study on small molecule acceptors, less attention has been paid on small molecule donors. Thus, it is meaningful and urgency to design and synthesis donor molecules since they play the same critical role compared to acceptors in the OSCs.

With the large absorption coefficients and broad spectral response range in visible region, porphyrin derivatives have been widely used in OSCs as the donor materials [39-41]. In 2015, Peng's group reported **DPPEZnP-TEH** [42], with a high short circuit current density (J_{sc}) and PCE of 16.76 mA/cm⁻² and 8.08%, respectively. In 2016, a high PCE of 9.06% [43] by DPPEZnP-TBO and PC₆₁BM when using the pyridine and 1,8-diiooctane (DIO) as the additives. Collaborating with Peng et al., we have reported a tandem cell using the porphyrin molecule DPPEZnP-TBO as the rear cell donor and achieved a PCE of 12.7% [9]. However, the above mentioned porphyrin based OSCs all employed fullerene derivatives as acceptors. Porphyrin molecules show broad and red-shifted absorption spectra in the visible and near-infrared region, whereas they have an absorption valley between Soret and Q band [44, 45]. If combining with an acceptor having complementary absorption with the porphyrin molecules, a nearly full spectrum of sunlight absorption would be realized for the active layers, which is a necessary prerequisite for designing of high efficiency OSCs. In fact, the recent result reported by Alex et al. has demonstrating promising results for all small molecule devices using a porphyrin donor and a NF small molecule [33].

In view of the above analysis, a porphyrin donor material **DEP-TT** has been synthesized and blended with a small molecule **IDT-C8** as the acceptor to fabricate all small molecule OSCs (Fig. 1). With strong electron donating ability and planar chemical structure, thieno[3,2-*b*] thiophene (TT) group is a good building block to construct OSCs molecules and has shown good results in literatures [46,47]. Considering the chemical structure and electron property of TT, we have introduced it on a center porphyrin unit and designed the molecule **DEP-TT** in order to

obtain red-shifted absorption and extended conjugation structure, which is desirable to have high current and good mobility in the OSC devices. **DEP-TT** exhibited a broad absorption region with an onset wavelength to 898 nm on the film and a low optical band gap of 1.31 eV. Considering the absorption valley around 600–700 nm of **DEP-TT**, we choose an A-D-A structure small molecule **IDT-C8** as acceptor, which has a strong absorption in range 500–750 nm on the solid film. The two small molecules exhibit not only complementary absorption but also matched energy levels. After devices optimization, a PCE of 5.14% was obtained for the **DEP-TT:IDT-C8** based OSCs. The detailed synthetic procedures (Fig. S1) and the corresponding characteristic data (¹H NMR, ¹³C NMR and HR-MS) of **DEP-TT** were summarized in the supporting information (SI). **DEP-TT** also showed good thermal stability up to 384 °C by thermogravimetric analysis under the nitrogen atmosphere (Fig. S2).

2. Result and discussion

2.1. Molecular design and synthesis

The synthetic routes of DEP-TT were displayed in Scheme 1. IDT-C8 was prepared according to literature procedures [48]. For synthesis of DEP-TT, intermediate 2 was prepared according to the reported literatures [46] and then subsequently brominated and reacted with zinc acetate to afford 3. The target molecule DEP-TT was synthesized via two steps Sonogashira coupling from 3. The detailed synthetic procedures are presented in the supporting information. The intermediate and the target molecules are well characterized by ¹H NMR, ¹³C NMR, FT-IR, melting point and HR-MS mass (see the details in the supporting information).

2.2. Photophysical and electrochemical properties

The electronic absorption spectra of **DEP-TT** in chloroform (CF) and on solid film were measured and the corresponding absorption properties are summarized in Table 1. As shown in Fig. 2a, in dilute chloroform solution, **DEP-TT** exhibits a broad absorption in the visible and nearinfrared region. It shows two intense absorption peaks located at 470 nm ($\varepsilon = 1.045 \times 10^5$ M⁻¹ cm⁻¹) and 565 nm ($\varepsilon = 0.978 \times 10^5$ M⁻¹ cm⁻¹), which are corresponding to the Soret band of typical porphyrin based molecules. Besides, DEP-TT also shows a strong absorption band with peak at 724 nm ($\varepsilon = 0.946 \times 10^5$ M⁻¹ cm⁻¹), which is attributed to the intramolecular charge transfer (ICT). In the solid state, the absorption range of Soret band remains nearly unchanged. But, the absorption



Fig. 1. Chemical structures of DEP-TT and IDT-C8.



Scheme 1. Synthetic route of DEP-TT.

 Table 1

 Photophysical and electrochemical data of DEP-TT and IDT-C8.

Compound	λ_{\max}^{CF} (nm)	$\lambda_{\max}^{\text{rmm}}$ (nm)	$\epsilon (10^{3} M^{-1} cm^{-1})$	Egor (eV)	HOMO (eV)	LUMO (eV)	Egv (eV)
DEP-TT	470	473	1.045	1.38	-4.81	-3.50	1.31
	565	572	0.978				
	724	788	0.946				
IDT-C8	668	711	1.963	1.52	-5.53	-3.79	1.74

band in the long wavelength redshifts clearly with a peak at 788 nm. The optical band gap based on the onset wavelength in the solid (898 nm) is 1.38 eV. The broad and redshift noted in the maxima in the thin film indicate an effective intermolecular π - π stacking in the solid state. As for **IDT-C8**, it has an intense absorption ranging from 550 nm to 750 nm in the thin film, which is complementary with that of **DEP-TT**.

Cyclic voltammetry measurements were performed in dichloromethane (DCM) solution containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte, with a scan rate of 100 mV s⁻¹ and calibrated with ferrocene (4.8 eV below vacuum). As shown in Fig. 3, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) were estimated from the onset oxidation or reduction potential to be -4.81 and -3.50 eV,



Fig. 2. UV-vis spectra of DEP-TT in chloroform (CF) solution and on the thin film (a) and the thin film absorption curves of DEP-TT and IDT-C8 (b).



Fig. 3. Cyclic voltammograms of DEP-TT recorded in DCM solution (a) and the energy levels (b).

respectively, for **DEP-TT**. The HOMO and LUMO of **IDT-C8** were estimated to be -5.53 and -3.79 eV, respectively, which are matched with those **DEP-TT** with the LUMO energy offset of 0.29 eV and HOMO energy offset of 0.72 eV.

2.3. OSCs performance

The OSC devices with a conventional structure of indium tinoxide ITO/PEDOT:PSS/**DEP-TT:IDT-C8**/(*N*,*N'*-bis(propylenedimethylamine)-3,4:9,10-perylenediimide) (PDINO)/Al were fabricated to evaluate the photovoltaic performance. The current density-voltage (*J*–*V*) curves (Fig. 4a) under different conditions were shown in Fig. 4a. The corresponding photovoltaic parameters are summarized in Table 2. For the as cast device, a low PCE of 0.64% with J_{sc} of 2.61 mA cm⁻², V_{oc} of 0.82 V and FF of 0.30 was obtained. Solvent vapor annealing (SVA) was used to fine-tune the morphology of the OSCs active layer. Four solvent, CF, dichloromethane (DCM), tetrahydrofuran (THF) and carbon disulfide (CS₂) were used for the SVA treatment. The best devices were obtained with SVA using tetrahydrofuran as solvent for 90 s. A significantly improved J_{sc} (from 2.61 to 11.15 mA cm⁻²) and fill factor (from 0.30 to 0.65) were achieved and the PCE increased from 0.64% to 5.14%.

The external quantum efficiencies (EQE) have been measured for further understanding the $J_{\rm sc}$ values for the devices under different conditions (Fig. 4b). All the devices showed broad photoelectric response in visible and near-infrared regions (from 300 nm to 900 nm). As shown in Fig. 4b, only a slightly increased EQE response was observed when the device was treated with SVA for 60 s compared with the as cast blend film based device. While an obvious enhancement of EQE was obtained for the device with SVA for 90 s (about 45% from 520 to 620 nm). The EQE decreased to around 35% (from 550 to 650 nm), especially with a trough of 14% in 388 nm when the SVA time increased to 120 s. The integrated $J_{\rm sc}$ values from EQE curves were 2.49, 3.86, 11.09 and 8.93 mA cm⁻², respectively, which accords well with the $J_{\rm sc}$ values from corresponding *J*-V curves with 4.6%, 4.0%, 0.5% and 2.1%

error, respectively.

The space-charge-limited-current (SCLC) (Fig. S2) method was used to evaluate the charge transport properties. The hole and electron mobility were 6.05×10^{-5} and 3.56×10^{-5} cm⁻² V⁻¹ s⁻¹, respectively for the as cast film. With the SVA treatment for 90 s by THF, the hole and electron mobility demonstrated the higher and more balanced hole and electron mobility of 8.42×10^{-5} and 5.01×10^{-5} cm⁻² V⁻¹ s⁻¹, respectively, which was favorable for the improvement of device FF.

The atomic force microscopy (AFM) and transmission electron microscopy (TEM) were used to investigate the film morphologies. As shown in Fig. 5a–d, the active layers without and with SVA at different time showed much smoother morphologies with root-mean-square (rms) surface roughness values of around 0.3 nm, indicating that SVA treatment has nearly no influence on the surface roughness. In the corresponding TEM images (Fig. 5e–h), the active layer with SVA for 90s (Fig. 5g) gave different phase separation with relatively moderate degree in contrast to those of the as cast and SVA 60s films. In the X-ray diffraction (XRD) images (Fig. S3), there are no obvious peaks for the as cast and SVA 90s blended films. However, sharp (100) peaks of **DEP-TT** and **IDT-C8** independent films were observed. It was proposed that the two small molecules might have good miscibility and thus lead to unfavorable separation, which contributed to the moderate J_{sc} of the OSC device.

3. Conclusions

In summary, we have fabricated an all small molecule OSC using a porphyrin derivative **DEP-TT** as donor and the small molecule **IDT-C8** as acceptor. The two small molecules showed complementary and broad absorptions in the range of 400–900 nm. After devices optimization, a PCE of 5.14% with V_{oc} of 0.71 V, J_{sc} of 11.15 mA cm⁻² and FF of 0.65 was achieved. The complementary and wide absorption ranges of the donor and acceptor molecules are the prerequisite to attain a high J_{sc} . In our case, the moderate J_{sc} was mainly attributed to the unfavorable



Fig. 4. The photocurrent density-voltage (J–V) curves (a) and EQE spectra of the as-cast and SVA treatment devices (b).

Table 2

Photovoltaic parameters for the DEP-TT:IDT-C8 based devices under	AM 1.5G	(100 mW cm^{-2})).
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SVA Time	$V_{\rm oc}(V)$	$J_{\rm sc} ({\rm mA~cm}^{-2})^{\rm a}$	FF	PCE _{max} (%)	PCE _{ave} (%) ^b	$J_{\rm sc}^{\rm EQE} ({\rm mA~cm}^{-2})^{\circ}$	error(%) ^d
w/o	0.82	2.61	0.30	0.64	$\begin{array}{c} 0.60 \pm 0.04 \\ 1.69 \pm 0.07 \\ 5.01 \pm 0.13 \\ 4.24 \pm 0.09 \end{array}$	2.49	4.6
60 s	0.72	4.02	0.61	1.76		3.86	4.0
90 s	0.71	11.15	0.65	5.14		11.09	0.5
120 s	0.71	9.12	0.67	4.33		8.93	2.1

^a the short-circuit current density caculated from the *J-V* curves.

 $^{\rm b}\,$ the PCE values were measured from 30 devices.

^c the short circuit-current density integrated from the EQE curves.

 $^{\rm d}\,$ the $J_{\rm sc}$ error between the caculated and the integrated ones.



Fig. 5. AFM height images (a, b, c and d) of the blend films based on DEP-TT and IDT-C8 with different SVA time. and the corresponding TEM images (e, f, g and h).

phase separations of the two small molecules. It is believed that high efficiency all small molecule OSCs could be obtained through the synergistic considerations of the active layer absorptions, energy levels and morphology control.

4. Experimental section

4.1. Materials and characterization techniques

All reactions and manipulations were carried out under argon atmosphere using the standard Schlenk techniques. All starting materials were purchased from commercial suppliers and used without further purification unless indicated otherwise. The ¹H and ¹³C nuclear magnetic resonance (NMR) spectra were taken on a Bruker AV400 Spectrometer. The HR-MS data were recorded on Varian 7.0T FT-MS. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA 409 PC instrument under purified argon gas flow. The heating rate for TGA testing is 15 °C min⁻¹, (DSC) UV–Vis spectra were obtained with a JASCO V-570 spectrophotometer. Cyclic voltammetry (CV) experiments were performed with a LK98B II microcomputer-based Electro-chemical Analyzer. All CV measurements were carried out at room temperature with a conventional three-electrode configuration employing a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and a Pt wire as the counter electrode. Dichloromethane was distilled from calcium hydride under dry nitrogen immediately prior to use. Tetrabutylammonium phosphorus hexafluoride (Bu_4NPF_6 , 0.1 M) in dichloromethane was used as the supporting electrolyte; the scan rate was 100 mV s^{-1} . Atomic force microscope

(AFM) was performed using MultiMode 8 atomic force microscope in tapping mode. The transmission-electron microscope (TEM) investigation was performed on Philips Technical G² F20 at 200 kV. SCLC mobility was measured using a diode configuration of ITO/PEDOT:PSS/ DEP-TT:IDT-C8/Au for hole and Al/DEP-TT:IDT-C8/Al for electron by taking the dark current density in the range of 0-2 V and fitting the results to a space charge limited form, where SCLC is described by:where J is the current density, L is the film thickness of the active layer, μ_0 is the hole or electron mobility, ε_r is the relative dielectric constant of the transport medium, ϵ_0 is the permittivity of free space (8.85 \times $10^{-12}~\text{F}$ m⁻¹), $V (= V_{appl} - V_{bi})$ is the internal voltage in the device, where V_{appl} is the applied voltage to the device and V_{bi} is the built-in voltage due to the relative work function difference of the two electrodes. The current density-voltage (J–V) curves of photovoltaic devices were obtained by a Keithley 2400 source-measure unit. The photocurrent was measured under illumination simulated 100 mW $\rm cm^{-2}\,AM$ 1.5G irradiation using a xen-on-lamp-based solar simulator [SAN-EI XES-70S1 (AM 1.5G)] in an argon filled glove box. External quantum efficiencies (EQE) were measured using Stanford Re-search Systems SR810 lock-in amplifier.

4.2. Synthesis of compound 2

A mixture of compound **1** (1.590 g, 4.049 mmol), dipyrromethane (592 mg, 4.049 mmol), in dichloromethane (DCM) (900 mL) was degassed with argon for 30 min. Then trifluoroacetic acid (270 μ L, 3.644 mmol) was injected into the reaction system. The reaction was stirred under argon atmosphere for 12 h, and then trifluoroacetic acid (1.378 g, 6.074 mmol) was added. The reaction was stirred from another

2 h and quenched with triethylamine (NEt₃) (5 mL). After removal of the solvent, the residue was redissolved in CH₂Cl₂. The organic phase was washed with water for three times and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum, and the crude product was purified by column chromatography using CH₂Cl₂/PE (1:2) as the eluent to give compound **2** as a purple solid. m.p. 202–205 °C. ¹H NMR (400 MHz, CDCl₃) δ 10.25 (s, 2H), 9.40 (d, *J* = 4.6 Hz, 4H), 9.35 (d, *J* = 4.6 Hz, 4H), 8.03 (s, 2H), 7.21 (s, 2H), 3.03 (d, *J* = 6.6 Hz, 4H), 1.87 (m, 2H), 1.48 (m, 14H), 1.37 (m, 34H), 0.95 (m, 12H), -3.01 (s, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 148.06, 147.28, 145.40, 141.71, 141.44, 137.33, 131.82, 131.13, 126.15, 117.11, 111.14, 106.10, 40.19, 35.80, 33.36, 31.99, 30.08, 29.76, 29.73, 29.41, 26.73, 22.75, 14.19, 14.17. IR (KBr) v: 3434, 3285, 2960, 2922, 2851, 2359, 2333, 1636, 1465, 1408, 1378, 1347, 1155, 1093, 975, 954, 799. HR-MS (MALDI): *m/z* [M]⁺ calcd for C₆₄H₈₂N₄S₄, 1034.5422, found, 1034.5424.

4.3. Synthesis of compound 3

A solution of N-bromosuccinimide (NBS) (113 mg, 0.638 mmol) in DCM (10 mL) was added dropwise to a solution of compound 2 (300 mg. 0.290 mmol) in CH₂Cl₂ (100 mL) and pyridine (5 mL) in the room temperature. The solution was stired for 3 h and quenched by acetone. After removal of the solvent, the residue was redissolved in CH₂Cl₂. The organic phase was washed with water for three times and dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was recrystallized by DCM/MeOH. After filtered under vacuum, a mixture of the crude product (290 mg, 0.243 mmol), (CH3COO)2Zn·2H2O (1067 mg, 4.860 mmol) in DCM (100 mL) and CH₃OH (5 mL) was stirred at room temperature for another 2 h. After removal of the solvent, the crude product was purified by column chromatography using CH₂Cl₂/ PE (1:1) as the eluent to afford compound 3 as purple solid. m.p. 148–153 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.29 (d, J = 4.6 Hz, 4H), 9.00 (d, J = 4.2 Hz, 4H), 7.80 (s, 2H), 7.15 (s, 2H), 3.02 (s, 4H), 1.87 (m, 2H), 1.47 (m, 14H), 1.42–1.33 (m, 32H), 0.99–0.91 (m, 14H). ¹³C NMR (101 MHz, CDCl₃) & 151.33, 149.86, 147.28, 142.10, 141.02, 136.87, 133.29, 132.99, 126.08, 116.96, 113.58, 105.63, 40.18, 35.79, 33.34, 32.03, 32.00, 30.11, 29.78, 29.76, 29.43, 26.73, 22.78, 22.76, 14.22, 14.19. IR (KBr) v: 3434, 2948, 2918, 2851, 1631, 1460, 1434, 1316, 1274, 1077, 1027, 1001, 778. HR-MS (MALDI): *m/z* [M]⁺ calcd for C₆₄H₇₈Br₂N₄S₄Zn, 1252.2768 found, 1252.2768.

4.4. Synthesis of compound 4

A mixture of compound 3 (300 mg, 0.239 mmol), trimethylsilylacetylene (117 mg, 1.195 mmol), CuI (14 mg, 0.0735 mmol), and Pd (PPh₃)₂Cl₂ (33 mg, 0.0470 mmol) in THF (25 mL) and NEt₃ (5 mL) was stirred and heated at 65 °C under a argon atmosphere for 12 h. After removal of the solvent, the residue was redissolved in CH₂Cl₂. The organic phase was washed with water for three times and dried over anhydrous Na₂SO₄. The solvent was removed under vacuum, and the crude product was purified by column chromatography using CH₂Cl₂/ PE (1:2) as the eluent to give compound 4 as a green solid. m.p. 55-60 °C. ¹H NMR (400 MHz, CDCl₃) δ 9.63 (d, J = 4.6 Hz, 4H), 9.22 (d, J = 4.6 Hz, 4H), 7.97 (s, 2H), 7.18 (s, 2H), 3.02 (d, J = 6.6 Hz, 4H), 1.86 (m, 2H), 1.46 (m, 14H), 1.35 (m, 32H), 1.01-0.88 (m, 14H), 0.61 (s, 18H). $^{13}\mathrm{C}$ NMR (101 MHz, CDCl3) δ 152.10, 150.77, 146.88, 142.06, 140.69, 136.64, 132.52, 131.18, 125.64, 116.71, 114.03, 106.63, 102.07, 101.90, 39.86, 35.46, 33.04, 31.70, 31.68, 29.77, 29.45, 29.42, 29.10, 26.41, 22.45, 22.44, 13.88, 13.87. IR (KBr) v: 3440, 2958, 2922, 2858, 2138, 1647, 1632, 1491, 1459, 1382, 1343, 1262, 1214, 1157, 1061, 880, 792, 711. HR-MS (MALDI): *m*/*z* [M]⁺ calcd for C₇₄H₉₆N₄S₄Si₂Zn, 1288.5348 found, 1288.5348.

4.5. Synthesis of compound DEP-TT

tetrabutylammonium fluoride (TBAF) (227 mg, 0.868 mmol), and THF 20 mL was stirred at room temperature for 15 min. 2 mL distilled water was added to quench the reaction. After removal of the solvent, the residue was redissolved in 50 mL CH₂Cl₂. The organic phase was washed with water for four times and dried over anhydrous Na₂SO₄. After the solvent was removed under vacuum, the crude product (100 mg, 0.0872 mmol) was transferred into a two-neck round bottomed flask. After that, a mixture of 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thiophen-2-yl)-pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (Br-DPP) (158 mg, 0.262 mmol), Pd₂(dba)₃ (8 mg, 0.00872 mmol), AsPh₃ (53 mg, 0.174 mmol) in THF (20 mL) and NEt3 (5 mL) was stirred and heated at 60 °C overnight under a argon atmosphere. After removal of the solvent, the crude product was purified by column chromatography using CHCl₃/PE (3:1) as the eluent to afford compound DEP-TT as a black solid (yield: 80%). m.p. 112–118 °C. ¹H NMR (400 MHz, CDCl₃/DMSO = 1/1) δ 9.03 (s, 4H), 8.90 (m, 4H), 8.87-8.79 (m, 2H), 8.73 (m, 2H), 8.19 (m, 2H), 7.75 (m, 2H), 7.38-7.25 (m, 6H), 3.94 (m, 4H), 3.58 (m, 4H), 3.14 (m, 4H), 1.99 (m, 2H), 1.86 (m, 2H), 1.78 (m, 2H), 1.57 (m, 15H), 1.41 (m, J = 20.3 Hz, 65H), 0.94 (m, 36H). IR (KBr) v: 3436, 2958, 2922, 2854, 2363, 2343, 2170, 1667, 1616, 1547, 1499, 1455, 1406, 1214, 1089, 1065, 788, 739, 703. HR-MS (MALDI): m/z [M]⁺ calcd for C128H156N8O4S8Zn, 2188.9307 found, 2188.9308.

Declaration of competing interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2020.108250.

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